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(54) EPOXY RESIN COMPOSITION AND HOLLOW PACKAGE FOR HOUSING SEMICONDUCTOR DEVICE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an epoxy resin composition with high thermal conductivity and excellent moisture resistance, suitable for a resin-made hollow package suppressing generation of metal impurities, and when preparing the resin composition, hardly abrasing the surface of rollers of a mixer or the surface of a screw by the inorganic filler in the composition, and to provide a resin-made hollow package using the composition.

SOLUTION: This epoxy resin composition comprises an epoxy resin, a curing agent, a spherical alumina powder and a low density spherical silica powder, and further comprises at least one selected from a spherical fused silica powder, a ground silica powder and an aluminum nitride powder. The spherical alumina powder has a sphericity of ≥0.9, an average particle diameter of ≥1 μm but <30 μm, and the content is 10-80 mass% in the total mass of the composition (provided that the total content of the inorganic filler is ≤95 mass% in the total mass of the composition). The thermal conductivity of the cured product of the composition is ≥1 W/mK.

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TI Epoxy resin compositions with high heat conductivity and moisture impermeability and hollow packages therefrom for semiconductor devices
IN Sakuraba, Tsukasa; Kondo, Masayuki; Togashi, Hideki
PA Mitsui Chemicals Inc., Japan
SO Jpn. Kokai Tokkyo Koho, 8 pp.
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DT Patent
LA Japanese
IC ICM C08L063-00
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CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 2003160714	ICM	C08L063-00
	ICS	C08K003-20; C08K003-28; C08K003-36; H01L023-08; H01L023-29; H01L023-31
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AB The compns. (heat conductivity ≥ 1W/m-K), useful for CCD or CMOS packages, comprise (A) epoxy resins, (B) curing agents and accelerators, (C) 10-80% of spherical Al2O3 powders [sphericity (definition is included) ≥0.9, average diameter ≥0.1 and <3 μm], and (D) low-d. spherical SiO2, and (E) other powders chosen from spherical fused SiO2, pulverized SiO2, and/or AlN with C + D + E ≤95%. The compns. have less contamination of metal impurities caused by apparatus wearing by hard inorg. fillers when kneading. Thus a composition containing EOCN 1020-70 (o-cresol novolak epoxy resin) 100, Milex XLC 3L [phenol-bis(methoxymethyl)benzene copolymer] 93, spherical Al2O3 1037, low-d. spherical SiO2 126, and fused spherical SiO2 302 parts was kneaded, showing heat conductivity 1.6 W/m-K, Fe content 240 ppm, and less Al mold abrasion. A transfer-molded hollow package from the composition was sealed with a glass lid, showing no dew formation after 10 h at 121° and 100% relative humidity.

ST spherical alumina low density silica filler epoxy package; semiconductor device hollow package metal free epoxy resin; cresol novolak epoxy hydroxy polybenzyl alumina silica package; CCD complementary MOS device epoxy hollow package

IT MOS devices
(complementary; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT Polybenzyls
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(epoxy, hydroxy-containing, novolak; metal-free epoxy resin compns. with

high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT Electronic packaging materials
(hollow packages; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT Charge coupled devices
Semiconductor devices
(metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT Epoxy resins, uses
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(polybenzyl-, hydroxy-containing, novolak; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT Fillers
(spherical; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT 25053-96-7DP, o-Cresol-formaldehyde copolymer, glycidyl ethers, polymers with hydroxy-containing polybenzyls
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(assumed monomers; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT 533864-03-8P
RL: IMF (Industrial manufacture); PRP (Properties); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT 7631-86-9, Silica, uses 24304-00-5, Aluminum nitride
RL: MOA (Modifier or additive use); TEM (Technical or engineered material use); USES (Uses)
(metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

IT 1344-28-1, Alumina, uses 60676-86-0, Fused silica
RL: MOA (Modifier or additive use); TEM (Technical or engineered material use); USES (Uses)
(spherical; metal-free epoxy resin compns. with high heat conductivity and moisture impermeability for hollow packages of semiconductor devices)

DERWENT-ACC-NO: 2004-102462

DERWENT-WEEK: 200413

TITLE: Epoxy resin composition for forming hollow package used for packaging semiconductor element, contains ball-shaped alumina powder having preset sphericity and mean particle diameter

PATENT-ASSIGNEE: MITSUI CHEM INC[MITA]

PRIORITY-DATA: 2001JP-0276132 (September 12, 2001) , 2001JP0047697 (February 23, 2001)

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ABSTRACTED-PUB-NO: JP2003160714A

BASIC-ABSTRACT:

NOVELTY - An epoxy resin composition contains an epoxy resin, a hardener, a hardening accelerator, a ball-shaped alumina powder, low-density ball-shaped silica powder, and ball-shaped fused silica powder, crushed silica powder and/or aluminum nitride powder. The ball-shaped alumina powder has sphericity of 0.9 or more, and mean particle diameter of 0.1-30 mu m.

DETAILED DESCRIPTION - An epoxy resin composition contains an epoxy resin, a hardener, a hardening accelerator, a ball-shaped alumina powder, a low-density ball-shaped silica powder and ball-shaped fused silica powder, crushed silica powder and/or aluminum nitride powder. The ball-shaped alumina powder has sphericity of 0.9 or more as calculated by the ratio of area with same periphery as the projection perimeter length of the project area to particle of perfect circle, and mean particle diameter of 0.1-30 mu m. The heat conductivity of cured epoxy resin composition is 1 W/m.K or more. The content of ball-shaped alumina powder is 10-85 mass%. The total amount of inorganic filler in the composition is 95 mass% or less.

An INDEPENDENT CLAIM is included for semiconductor element accommodating hollow package (1).

USE - For forming hollow package for semiconductor element (claimed) used for charge coupled device and complementary metal oxide semiconductor.

ADVANTAGE - The epoxy resin composition has excellent moisture resistance and heat conductivity.

DESCRIPTION OF DRAWING(S) - The figure shows the sectional drawing of hollow package formed by molding epoxy resin composition.

hollow package 1

CHOSEN-DRAWING: Dwg.1/2

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the semiconductor device receipt hollow package which consists of an epoxy resin constituent and this resin constituent excellent in thermal conductivity suitable as an object for the hollow package for containing a semiconductor device, and moisture resistance and a moldability.
[0002]
[Description of the Prior Art] The cheap package made of resin is used for the hollow package for containing solid state image sensors, such as CCD (Charge Coupled Device) and CMOS (Complementary Metal Oxide Semiconductor), conventionally besides the ceramic. Generally the hollow package made of resin has connected electrically the leadframe which was united with the resin Plastic solid by insert molding and by which both ends were opened wide on the inside and the outside of a package, and the semiconductor device which fixed with adhesives in the package center section by the bonding wire. Moreover, the top face of a resin Plastic solid fixes lid material, such as a transparent synthetic-resin plate and a glass plate, with adhesives, and has hermetic seal structure.
[0003] While a raise in the pixel of image recording devices, such as a video camera carrying such a hollow package made of resin and a digital camera, and a miniaturization demand increase in recent years, the military requirement to solid state image sensors, such as CCD and CMOS, is also increasing. That is, with progress of a raise in a pixel, and a miniaturization, the calorific value of a semiconductor device increases and there is a possibility of making the function of the image sensor itself falling by this. Therefore, the hollow package made of resin with the high heat conductivity is demanded by raising the heat dissipation nature from the material of a hollow package that such a problem should be solved.
[0004] Although the approach of adding the inorganic bulking agent which has high temperature conductivity including alumina powder as a means which raises the thermal conductivity of a resin moldings, and preparing with heating melting kneading machines, such as 2 rolls, a kneader, or an extruder, is used conventionally These inorganic bulking agents had the high degree of hardness, since the configuration of the letter of crushing was generally carried out, the roll surface and screw front face of a kneading machine were remarkably worn out at the time of kneading, and the problem which a metal impurity mixes into a resin constituent was pointed out.
[0005] Moreover, since the thickness of a resin Plastic solid became thin in connection with it by one side when a package is miniaturized, the point that the moisture in atmospheric air became easy to infiltrate into the interior of a package through a resin Plastic solid was also made into the problem.
[0006]
[Problem(s) to be Solved by the Invention] About the epoxy resin constituent which was proposed in order that this invention might solve said trouble, and contained the inorganic bulking agent Thermal conductivity is higher than the conventional thing, and it excels in moisture resistance. Further In the case of preparation of a resin constituent It is rare to wear the roll surface and screw front face of a

kneading machine with the inorganic bulking agent in a constituent. It is in offering the suitable epoxy resin constituent for the hollow package made of resin which suppressed generating of a metal impurity, and offering the hollow package made of resin for containing solid state image sensors, such as a raise in a pixel, CCD to miniaturize, and CMOS, increasingly from now on.
[0007]
[Means for Solving the Problem] this invention persons came to complete the invention in this application, as a result of examining many things, in order to solve the above-mentioned technical problem. Namely, this invention contains a ** epoxy resin, a curing agent, a hardening accelerator, spherical alumina powder, and low consistency spherical silica powder. In addition, it is an epoxy resin constituent containing at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder. 0.9 or more and mean particle diameter the above-mentioned spherical alumina powder 0.1 micrometers or more less than 30 micrometers, [the degree of sphericity for which it asked by following the (1) formula] And the content to the total mass of a constituent is below 80 mass % more than 10 mass % (however, with spherical alumina powder and low consistency spherical silica powder). the content of at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder of sum totals is below 95 mass % to the total mass of a constituent. The epoxy resin constituent characterized by the thermal conductivity of the hardened material of this constituent being 1 or more W/m-K is offered.
Degree of sphericity = area with the same periphery as the projection boundary length of the projected area/particle of a particle of a perfect circle -- (1) [0008] ** For 3% or more and mean particle diameter, the consistencies of an epoxy resin constituent given in the aforementioned ** to which it is characterized by 0.1-micrometer or more thing which it is less than 3 micrometers and is contained below 30 mass % more than 1 mass % in [all] a constituent in which said low consistency spherical silica powder measured 1-butanol as a medium are [less than three 2.10 g/cm and moisture absorption] modes with desirable this invention.
[0009] Moreover, the epoxy resin constituent for a semiconductor device receipt hollow package characterized by this invention becoming the ** aforementioned ** or ** from the epoxy resin constituent of a publication is offered.
[0010] Moreover, the semiconductor device receipt hollow package characterized by this invention being fabricated by the ** aforementioned ** or ** from the epoxy resin constituent of a publication is offered.
[0011]
[Embodiment of the Invention] This invention is explained below at a detail. The epoxy resin constituent of this invention is an epoxy resin constituent whose thermal conductivity of a hardened material is 1 or more W/m-K including at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder in addition including an epoxy resin, a curing agent, a hardening accelerator, spherical alumina powder, and low consistency spherical silica powder.
[0012] As an epoxy resin of <epoxy resin> this invention, each epoxy resin of the bisphenol A mold, a bisphenol female mold, and the bisphenol A D mold, a phenol novolak mold epoxy resin, polyglycidyl ether of o-cresol-form aldeyde novolac, a naphthalene frame content epoxy resin, and a biphenyl frame content epoxy resin are used suitably, any these one kind may be used independently, or two or more kinds may be used together by the suitable ratio. As for the weight per epoxy equivalent of these epoxy resins, below 300 (g/eq) is desirable, and more than below further 300 (g/eq) 100 (g/eq) is desirable. It sets to this invention, and it is below 30 mass % more than 2 mass %, and, as for the loadings in all the resin constituent of an epoxy resin, it is usually desirable that it is especially in within the limits below 15 mass % more than 3 mass %.
[0013] Although it can be especially used without a limit as a curing agent used by <curing agent> this invention if a hardening reaction is carried out with the above-mentioned epoxy resin, especially, phenol resin is desirable and, specifically, phenol novolak resin and aralkyl phenol resin are mentioned. Moreover, acid dihydrazide, such as acid anhydrides, such as amines, such as diamino diphenylmethane, diaminodiphenyl sulfone, and m-phenylenediamine, phthalic anhydride, an anhydrous tetrahydrophtal

acid, and anhydrous hexahydrophthalic acid, isophthalic acid dihydrazide, and adipic-acid dihydrazide, a dicyandiamide, a boron trifluoride, etc. are mentioned as a suitable thing.
[0014] As for the loadings of a curing agent, it is desirable that the chemical equivalent ratio to the epoxy group of an epoxy resin is in the range of 0.5-1.5 from a viewpoint of moisture resistance and a mechanical property, and it is desirable that it is in a pan in the range of 0.7-1.2.
[0015] As a hardening accelerator used by <hardening-accelerator> this invention, what promotes the crosslinking reaction of said epoxy resin and curing agent is used. As the concrete example, 2-methylimidazole, 2-ethyl-4-methylimidazole, Imidazole derivatives, such as a 2-ethyl-4-methylimidazole azine; organic phosphines;1, such as triphenyl phosphine and the Tori (p-methylphenyl) phosphine, 8-diaza cyclo (5, 4, 0) undecene -7 (it is called Following DBU.) DBU derivative; type Ar-NH-CO-NR2, such as a phenol salt, a phenol novolak salt, and a carbonate, and Ar-(NH-CO-NR2) 2 (Ar -- a permutation or an unsubstituted aryl group --) R is the same, the permutation which may differ, or an unsubstituted alkyl group. The urea derivative expressed is mentioned.
[0016] As for a hardening accelerator, it is desirable to be blended below in 20 mass sections more than the 0.1 mass sections to the epoxy resin 100 mass section, and it is desirable to be blended with a pan at a rate below 10 mass sections more than the 0.1 mass section.
[0017] As an inorganic bulking agent used for <inorganic bulking agent> this invention, at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder in addition is included including spherical alumina powder and low consistency spherical silica powder.
[0018] The degrees of sphericity for which it asked by following the (1) formula are 0.9 or more things, mean particle diameter is 0.1-micrometer or more less than 30-micrometer thing, and the spherical alumina powder used by this invention is 0.5-micrometer or more less than 30-micrometer thing preferably. Degree of sphericity = area with the same periphery as the projection boundary length of the projected area/particle of a particle of a perfect circle -- (1) In order to ask for a degree of sphericity, measure by performing image analysis of the SEM photograph acquired with the electron microscope using a scanning electron microscope and image-analysis equipment. A measurement particle number is 100 or more pieces. Mean particle diameter was measured with the laser diffraction type particle-size-distribution measurement machine. Moreover, as long as a degree of sphericity is the thing of this range, the alumina powder of two or more classes may be used. In this case, the mean particle diameter of the alumina powder which mixed the alumina powder of two or more classes is within the limits of the above. As for a maximum grain size, it is desirable that it is 200 micrometers or less.
[0019] While the thermal conductivity of an epoxy constituent becomes high by using such spherical alumina powder, in the case of preparation of a resin constituent, it is rare to wear the roll surfaces and screw front faces of a kneading machine, such as a roll of two, a kneader, or an extruder, and it can reduce generating of a metal impurity sharply compared with the letter alumina powder of crushing currently used conventionally. In this invention, the content to the total mass of the constituent of spherical alumina powder is below 80 mass % more than 10 mass %, and is below 80 mass % more than 25 mass % preferably. However, the content of at least one sort chosen from spherical alumina powder and low consistency spherical silica powder, spherical fused silica powder and crushing silica powder, and alumimium nitride powder of sum totals is below 95 mass % to the total mass of a constituent, and it is preferably desirable that it is below 95 mass % more than 30 mass %. While excelling that it is this range in the moldability of an epoxy resin constituent, the property of resin hardened materials, such as a mechanical strength, is maintained.
[0020] The low consistency spherical silica powder used by this invention has that desirable whose consistencies which measured 1-butanol as a medium are less than three 2.10 g/cm, and what is three or less 2.05 g/cm is [three or more] desirable further 1.55 g/cm. As for moisture absorption, what is 3% or more is desirable, and what is 5 more% or more is desirable. Moreover, 0.1-micrometer or more thing which is less than 3 micrometers of mean particle diameter is desirable, and its 0.2 more micrometer or more less than 3-micrometer thing is desirable.
[0021] In this invention, the consistency of low consistency spherical silica powder was measured by the following approach. Silica about 5g which fully ground to the WADON mold specific gravity bottle

(mass m0) with a capacity of 50ml specified by JISR3503, and was dried to it was put in and weighed precisely. Sum total mass of the specific gravity bottle at this time and a silica was set to mS. 1-butanol about 10ml deaerated beforehand was added, and ultrasonic stirring was performed for 30 minutes. Subsequently, this specific gravity bottle is moved to a vacuum desiccator, it permeated in for [every] 15 minutes into the degree of vacuum of 30mmHg(s), and 1-butanol was made to permeate a silica enough at least. next, 1-butanol -- a specific gravity bottle -- filling -- a lid -- carrying out -- 25-degree C constant temperature -- mass was measured after making a phase carry out immersion neglect for 15 minutes. Sum total mass of the specific gravity bottle, the silica, and 1-butanol at this time was set to mS1.

[0022] Moreover, apart from this, the next actuation was performed in order to measure the volume of a specific gravity bottle. Mass was measured, after having filled the water which carried out degassing processing beforehand to the specific gravity bottle, covering and making a 25-degree C constant temperature bath carry out immersion neglect for 15 minutes. Sum total mass of the specific gravity bottle and water at this time was set to m1. And consistency rhoS of the silica in 25 degrees C was computed with the following calculus.

rhoS=(mS-m0)/{V-(mS1-mS)/rhoB}

however, V=(m1-m0)/rhoW -- here -- the mass (g) of an m0:specific gravity bottle

mS: Sum total mass of a specific gravity bottle and a silica (g)

mS1: Sum total mass of a specific gravity bottle, a silica, and 1-butanol (g)

m1: Sum total mass of a specific gravity bottle and water (g)

rhoS: The consistency of the silica in 25 degree C (g/cm3)

rhoB: The consistency of the 1-butanol in 25 degree C (0.8060 g/cm3)

rhoW: The consistency of the water in 25 degree C (0.997047 g/cm3)

V: Volume of a specific gravity bottle (cm3)

It comes out. In addition, measurement computed the average repeatedly twice.

[0023] In this invention, the moisture absorption of low consistency spherical silica powder was measured by the following approach. Silica about 5g fully dried is put into a container, and is weighed precisely, and mass at this time is set to W0. subsequently, this container -- the constant temperature of 60 degrees C and 90%RH (relative humidity) -- it puts into a constant humidity chamber, and is left for 24 hours, and mass at this time is set to W1. Moisture absorption was calculated from this W0 and W1 by the following formula.

Moisture absorption (%) ={(W1-W0) /W0} x100[0024] In this invention, the mean particle diameter of low consistency spherical silica powder was measured by the following approach. The ultrasonic agitator was used for a dispersion medium 10 thru/or 20ml, and it was made to distribute a silica 5 thru/or 50mg. As a dispersion medium, water or a polyethylene glycol was used according to particle size. Dispersion liquid were moved to the cel, and it covered except for air bubbles, and applied to the centrifuge particle-size-distribution measurement machine (Horiba CAPA-700 mold). Rotational speed of a measurement machine was set to 500 thru/or 5000rpm according to particle size. D (MEDIAN) value computed by the measurement machine was made into mean particle diameter. Moreover, in addition to this in mean-particle-diameter measurement of this invention, it measured also with the electron microscopic method and the laser diffraction method according to particle size.

[0025] Even if the hollow package made of resin is miniaturized and the thickness of a Plastic solid becomes thin by using such low consistency globular form silica powder, it has moisture resistance to the penetration to the package of the moisture in atmospheric air. As for the content in all the constituents of low consistency spherical silica powder, it is desirable that it is below 30 mass % more than 1 mass %, and it is desirable that it is below 20 mass % more than 1 mass % further.

[0026] If spherical fused silica powder is spherical fused silica powder, especially the degree of sphericity will not be limited. 0.1-micrometer or more less than 40-micrometer thing of mean particle diameter is desirable, and its 1 more micrometer or more less than 35-micrometer thing is desirable. Crushing silica powder may be fused silica, or may be a crystal silica. 0.1-micrometer or more less than 35-micrometer thing of mean particle diameter is desirable, and its 1 more micrometer or more less than

30-micrometer thing is desirable. The mean particle diameter of alumimium nitride powder has desirable 0.1-micrometer or more less than 30-micrometer thing, and 0.1 more micrometer or more less than 20-micrometer thing is used preferably. It is chosen in order that the inorganic filler of such spherical fused silica powder, crushing silica powder, and alumimium nitride powder may control the thermal conductivity of a hardened material, and loadings are adjusted.

[0027] In <other compounding agent> this invention, if needed, it is the range which does not spoil the purpose of this invention, and ferrite powder, aluminum-hydroxide powder, calcium-carbonate powder, etc. can be combined as other inorganic fillers. Moreover, metallic soap, such as metal salt; zinc stearate of higher fatty acids, such as ester wax; KARUNABA wax (carnauba wax); behenic acid zinc of higher fatty acids, such as a montanoic acid, stearin acid, behenic acid, and oleic acid, zinc oleate, magnesium stearate, barium stearate, and aluminum stearate, can be combined as a release agent. Even if these are independent, and it mixes and uses, they do not interfere.

[0028] Moreover, even if it blends coloring agents, such as flame retarders, such as a silane coupling agent, a bromine-ized epoxy resin, and an antimony trioxide, carbon black, and a phthalocyanine, and a low stress-ized agent if needed to this resin constituent in addition to these, it does not interfere. In this invention, after mixing all these ingredients with mixers usually used, such as a Henschel mixer, the epoxy resin constituent made into the purpose by carrying out heating kneading by 2 rolls, a kneader, etc., and cooling and grinding continuously is obtained.

[0029] Although this epoxy resin constituent shows the fitness which was excellent as an object for the hollow package for containing solid state image sensors, such as CCD and CMOS, it is natural. [of the ability to be used for the semi-conductor closure for which an epoxy resin constituent is generally used, electronic parts, etc.]

[0030] As the hollow package fabricated with the epoxy resin constituent of <hollow package> this invention is usually shown in drawing 1 , it consists of a configuration 1 of the cube type in which the upper part carried out opening, and the top face is sealed by the lid material 2, such as glass and transparent plastics, through adhesives 3. Furthermore, an island 4 is established in a package central crevice, and the semiconductor device 5 laid there is connected with a leadframe through a bonding wire 6. A leadframe is really fabricated by insert molding at the time of package shaping, and is connected through the leadframe by which the external lead 7 and the internal lead 8 were enclosed in the package.

[0031] Although the semiconductor device receipt hollow package of this invention is fabricated by the shaping approach of arbitration, such as an injection-molding method and a transfer-molding method, using the aforementioned epoxy resin constituent, a transfer-molding method is adopted preferably. When based on the transfer-molding approach, it can fabricate according to the pressure of one to 50x106Pa (10-500kg/cm2), the temperature of 150-200 degrees C, and the process condition for [time amount] 1 - 5 minutes.

[0032]

[Example] Although an example explains hereafter the effectiveness which was excellent in this invention, this invention is not limited to an example.

[0033] (Examples 1-5, examples 1-4 of a comparison)

All the raw material orthochromatic cresol novolak epoxy resins shown in Table 1 <an epoxy resin> : The Nippon Kayaku Co., Ltd. make, EOCN-1020-70, weight-per-epoxy-equivalent =205g /, and eq, aralkyl phenol resin <a curing agent> : The Mitsui Chemicals, Inc. make, MIREKKUSU XLC-3L, an imidazole <a hardening accelerator> : Made in Shikoku Chemicals, 2E4 MZ-AZINE and spherical alumina powder (1) < inorganic filler > : The mean particle diameter of 9.0 micrometers, Consistency 3.57 g/cm3, a degree of sphericity 0.92, the spherical alumina powder (2) <: [inorganic bulking agent >] (a) mean particle diameter of 45 micrometers, Consistency 3.98 g/cm3, the thing and (b) mean particle diameter of 4 micrometers of a degree of sphericity 0.92, (a)/(b)/(c) =5/3/2 mixed comparatively (mass ratio) three kinds of the thing of consistency 3.98 g/cm3, and the thing of (c) mean particle diameter of 0.7 micrometers, and consistency 3.98 g/cm3. The mean particle diameter of 14 micrometers, spherical alumina powder of consistency 3.98 g/cm3, letter alumina powder of crushing <an inorganic filler> : The mean particle diameter of 12.0 micrometers, Consistency 3.98 g/cm3, low consistency spherical

silica powder <an inorganic filler> : The mean particle diameter of 1.0 micrometers (centrifuge particle-size-distribution measurement machine), Consistency (medium 1-butanol) 1.78 g/cm3, 11.8% of moisture absorption, spherical fused silica powder < inorganic filler >: -- the mean particle diameter of 26.0 micrometers, consistency 2.21 g/cm3, and the crushing silica powder <inorganic filler>:mean particle diameter of 14.5 micrometers Consistency 2.65 g/cm3, alumimium-nitride powder <an inorganic filler>: Mean particle diameter of 0.5 micrometers, consistency 3.26 g/cm3 (the mean particle diameter of inorganic fillers other than low consistency spherical silica powder), it measured with the laser diffraction type particle-size-distribution measuring device Granulometer MODEL920 made from CILAS, and the value of the specific gravity measured by the pycnometer was shown in the consistency according to the approach defined by JIS.
Montanoic acid wax <a release agent> : Made in Clariant Japan, RIKOWAKKUSU OP, Silane-coupling-agent <Flame-retarder>: The Shin-Etsu Chemical Co., Ltd. make, KBM-403, a bromine-ized epoxy resin <a flame retarder> : The Nippon Kayaku Co., Ltd. make, BREN-S, weight-per-epoxy-equivalent =285 g/eq, an antimony trioxide <a flame retarder> : The NIHON SEIKO CO., LTD. make, PATOX-M, carbon black <a coloring agent>: After mixing the Mitsubishi Chemical make and #45 with a Henschel mixer at a rate of the weight section of a publication to front Naka, heating kneading was carried out with 2 rolls with a temperature of 90-110 degrees C, subsequently cooling grinding was carried out, and the epoxy resin constituent was obtained. Physical properties were measured by the following evaluation approaches using this constituent. The result was collectively shown in Table 1.
[0034] Using the metal mold with which the interior according to <evaluation approach> (1) spiral-flow EMMI1-66 specification became spiral-like, it fabricated in transfer molding by the die temperature of 150 degrees C, and the effective pressure of 6.9x106Pa (70 kgf/cm2), and the die length within the metal mold when hardening for 180 seconds which flowed was measured.
[0035] (2) It measured using the quick thermal conductivity meter by thermal conductivity Kyoto Electronics Manufacturing Co., Ltd. first, the epoxy resin constituent which is the above, and was made and prepared -- 105mm(L) x55mm(W) x -- it fabricated in the size of 15mm (H), and this Plastic solid was left in the 23-degree C ambient atmosphere for 12 hours or more. Next, the probe of a quick heat-conductivity meter was put on the Plastic solid, the value of 1 minute after was read, and it considered as the heat conductivity.
[0036] (3) metal high impurity concentration -- Fe concentration contained in a constituent as an impurity in the epoxy resin constituent prepared as mentioned above using the inductively-coupled-plasma-atomic-emisson-spectroscopy equipment made from Leeman Labs was measured. This Fe concentration was made into the standard of the wear degree on the front face of a kneading machine at the time of kneading.
[0037] (4) Although proposed from each company, since the evaluation approach of metal mold abrasiveness metal mold abrasiveness had many which carry out a long duration important point to measurement, it performed the abrasion test to the metal mold made from aluminum as a promoting method. It pressurized by the pressure of 7.8x106Pa (80 kgf/cm2) after supplying to the metal mold which heated the epoxy resin constituent specifically prepared as mentioned above using the metal mold shown in drawing 2 at 90 degrees C, and 19 cc was made to breathe out from a tip hole with a diameter [of the nozzle made from aluminum] of 2mm. Then, the bore of a nozzle tip hole was measured by the coordinate measuring machine, and the abrasion loss inside the tip hole produced by having made the constituent breathe out (volume) was computed. This value as well as the above-mentioned (3) metal high impurity concentration was made into the criterion of the wear degree on the front face of a kneading machine.
[0038] (5) In the condition of a specific heat hollow package, since measurement of heat conduction by the probe method was impossible, it considered as the thermally conductive standard as a package with the specific heat of mold goods. the mold goods fabricated according to the hollow package process condition of said paragraph number [0031] to a dimension -- about 3 -- the test piece whose weight is about 5mg in the magnitude which is mmx3mm -- starting -- the PerkinElmer, Inc. make -- it measured using DSC-7. The temperature up of the specific heat was carried out the rate for 10-degree-C/from

ordinary temperature, and it showed the value at the time of 40 degrees C.
[0039] (6) moisture resistance -- fabricate the epoxy resin constituent prepared as mentioned above by transfer molding, and fabricate a hollow package "A" according to the pressure of 7x106Pa (70kg/cm2), the temperature of 180 degrees C, and the process condition for [time amount] 2 minutes. Next, in order to carry out the hermetic seal of the centrum, the lid material "a" which applied UV hardening adhesives to the glass plate is prepared, "a" which turned the adhesives spreading side to "A" down is put, and UV hardening is carried out. In this way, the specimen of the hollow which carried out the hermetic seal was obtained, and moisture resistance was evaluated by measuring the moisture content which infiltrates into a centrum. Measurement referred to the approach indicated by the television society magazine (42 (9) 959 (1988)). Namely, the specimen was put into the pressure cooker testing machine, and was exposed for 10 hours in the wet heat environment of the temperature of 121 degrees C, and 100% of humidity RH. Subsequently, forced cooling of the glass side was carried out, and it investigated whether the moisture in a centrum would dew. What dew condensation was not accepted in with a pressure cooker was judged to be O.
[0040]
[Table 1]

原料 (重量部)		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5	比較例 1	比較例 2	比較例 3	比較例 4
オルソクレゾールノボラックエポキシ樹脂		100	100	100	100	100	100	100	100	100
アラルキルフェノール樹脂		93	93	93	93	93	93	93	93	93
ブロム化エポキシ樹脂		27	27	27	27	27	27	27	27	27
無機充填剤	球状アルミナ粉(1)	1037	518	1037	1037					
	球状アルミナ粉(2)					724				
	破砕状アルミナ粉						1037		518	
	低密度球状シリカ粉	126	126	126	126	137	126	126	126	126
	球状溶融シリカ粉	302	593				302		593	1339
	破砕シリカ粉			302		724		1339		
	窒化アルミニウム粉				302					
三酸化アンチモン		5	5	5	5	5	5	5	5	5
カーボンブラック		2	2	2	2	3	2	2	2	2
シランカップリング剤		7	7	7	7	3	7	7	7	7
イミダゾール		7	7	7	7	7	7	7	7	7
モンタン酸ワックス		3	3	3	3	3	3	3	3	3
スパイラルフロー (cm)		72	60	48	30	23	34	29	39	77
熱伝導率 (W/m·K)		1.6	1.1	2.0	2.5	2.4	2.2	1.8	1.2	0.8
金属不純物濃度 (Fe) (ppm)		240	180	350	380	470	1750	1130	860	200
金型摩耗量 ($\times 10^{-3}$cc)		0.44	0.39	0.58	0.65	1.04	3.50	2.70	2.10	0.40
耐湿性		O	O	O	O	O	O	O	O	O
パッケージ成形品の比熱 ($\times 10^{-1}$J/g°C)		9.28	未測定	未測定	未測定	未測定	未測定	未測定	未測定	9.95

[0041] The epoxy resin constituent (examples 1-4) which blended spherical alumina powder shows the heat conductivity of 1 or more W/m-K, and since the specific heat of package mold goods is also small, thermal conductivity is superior to the result of Table 1. Moreover, the value also with the low concentration of a metal impurity was shown, and since there was also little metal mold abrasion loss compared with the constituent (examples 1-3 of a comparison) which made the subject crushing alumina powder and crushing silica powder, it turned out that there are few damages on the front face of a kneading machine. The result also with still better moisture resistance was shown. The example 4 of a comparison was the constituent of only spherical silica powder, and although there were little metal high

impurity concentration and metal mold abrasion loss, thermal conductivity turned around 1 W/m-K the bottom.

[0042]

[Effect of the Invention] The epoxy resin constituent of this invention is excellent in moisture resistance, and its thermal conductivity is high and it fits the hollow package made of resin for containing solid state image sensors, such as CCD and CMOS. Furthermore, the wear on the kneading-machine roll surface at the time of preparing a constituent or the front face of a screw made into the trouble of an inorganic bulking agent of giving high temperature conductivity including the alumina of the letter of crushing, and the point of mixing of a metal impurity are remarkably improvable.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1] An epoxy resin, a curing agent, a hardening accelerator, spherical alumina powder, and low consistency spherical silica powder are included. In addition, it is an epoxy resin constituent containing at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder. 0.9 or more and mean particle diameter the above-mentioned spherical alumina powder 0.1 micrometers or more less than 30 micrometers, [the degree of sphericity for which it asked by following the (1) formula] And the content to the total mass of a constituent is below 80 mass % more than 10 mass % (however, with spherical alumina powder and low consistency spherical silica powder). the content of at least one sort chosen from spherical fused silica powder, crushing silica powder, and alumimium nitride powder of sum totals is below 95 mass % to the total mass of a constituent. The epoxy resin constituent characterized by the thermal conductivity of the hardened material of this constituent being 1 or more W/m-K.
Degree of sphericity = area with the same periphery as the projection boundary length of the projected area/particle of a particle of a perfect circle -- (1) [Claim 2] The epoxy resin constituent according to claim 1 with which less than three 2.10 g/cm and moisture absorption are characterized [the consistency in which said low consistency spherical silica powder measured 1-butanol as a medium] by 0.1-micrometer or more thing which it is less than 3 micrometers and is contained below 30 mass % more than 1 mass % in [all] a constituent by 3% or more and mean particle diameter.
[Claim 3] The epoxy resin constituent for a semiconductor device receipt hollow package characterized by consisting of an epoxy resin constituent according to claim 1 or 2.
[Claim 4] The semiconductor device receipt hollow package characterized by being fabricated from an epoxy resin constituent according to claim 1 or 2.

[Translation done.]

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(54)【発明の名称】　エポキシ樹脂組成物およびそれを用いた半導体素子収納中空パッケージ

(57)【要約】
【課題】　熱伝導率が高く、耐湿性に優れ、さらに樹脂組成物の調製の際、混練機のロール表面やスクリュ表面を組成物中の無機充填剤によって摩耗させることが少なく、金属不純物の発生を抑えた樹脂製中空パッケージ用に好適なエポキシ樹脂組成物およびそれを用いた樹脂製中空パッケージを提供する。
【解決手段】　エポキシ樹脂組成物は、エポキシ樹脂、硬化剤、硬化促進剤、球状アルミナ粉および低密度球状シリカ粉を含み、加えて球状溶融シリカ粉、破砕シリカ粉および窒化アルミニウム粉から選ばれる少なくとも１種を含む組成物であって、上記球状アルミナ粉は球形度が０．９以上、平均粒径が０．１μｍ以上３０μｍ未満、かつ組成物の全質量に対する含有量が１０質量％以上８０質量％以下であり（但し、前記無機充填剤の合計の含有量は、組成物の全質量に対して９５質量％以下である。）、該組成物の硬化物の熱伝導率が１Ｗ／ｍ・Ｋ以上であることを特徴とする。

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【特許請求の範囲】

【請求項1】　エポキシ樹脂、硬化剤、硬化促進剤、球状アルミナ粉および低密度球状シリカ粉を含み、加えて球状溶融シリカ粉、破砕シリカ粉および窒化アルミニウム粉から選ばれる少なくとも1種を含むエポキシ樹脂組成物であって、上記球状アルミナ粉は下記（1）式で求めた球形度が0．9以上、平均粒径が0．1μm以上30μm未満、かつ組成物の全質量に対する含有量が10＊

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【請求項2】　前記低密度球状シリカ粉が、1－ブタノールを媒体として測定した密度が2．10g／cm^{3}未満、吸湿率が3％以上、かつ平均粒径が0．1μm以上3μm未満であり、全組成物中に1質量％以上30質量％以下含有されることを特徴とする請求項1に記載のエポキシ樹脂組成物。

【請求項3】　請求項1または2に記載のエポキシ樹脂組成物からなることを特徴とする半導体素子収納中空パッケージ用エポキシ樹脂組成物。

【請求項4】　請求項1または2に記載のエポキシ樹脂組成物から成形されたことを特徴とする半導体素子収納中空パッケージ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、半導体素子を収納するための中空パッケージ用として好適な熱伝導性と、耐湿性、成形性に優れたエポキシ樹脂組成物および該樹脂組成物からなる半導体素子収納中空パッケージに関する。

【0002】

【従来の技術】従来、CCD（Charge Coupled Device）やCMOS（Complementary Metal Oxide Semiconductor）等の固体撮像素子を収納するための中空パッケージには、セラミックの他に、廉価な樹脂製パッケージが用いられている。一般的に樹脂製中空パッケージは、インサート成形によって樹脂成形体と一体化された、両端がパッケージの内側と外側に開放されたリードフレームと、パッケージ中央部に接着剤によって固着された半導体素子とを、ボンディングワイヤーにより電気的に連結している。また、樹脂成形体の上面は、透明な合成樹脂板、ガラス板等の蓋材を接着剤によって固着し、気密封止構造になっている。

【0003】近年、このような樹脂製中空パッケージを搭載するビデオカメラ、デジタルカメラ等の映像記録装置の高画素化、小型化要求が高まる中で、CCDやCMOS等の固体撮像素子に対する要求性能も高まりつつある。すなわち、高画素化、小型化の進展にともない、半導体素子の発熱量が増加し、これによって、撮像素子自体の機能を低下せしめる恐れがある。そのため、中空パッケージの素材からの放熱性を高めることによりこのよ※

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＊質量％以上80質量％以下であり（但し、球状アルミナ粉および低密度球状シリカ粉と、球状溶融シリカ粉、破砕シリカ粉、窒化アルミニウム粉から選ばれる少なくとも1種との合計の含有量は、組成物の全質量に対して95質量％以下である。）、該組成物の硬化物の熱伝導率が1W／m・K以上であることを特徴とするエポキシ樹脂組成物。

※うな問題を解決すべく、熱伝導率の高い樹脂製中空パッケージが要望されている。

【0004】従来、樹脂成形物の熱伝導率を向上させる手段としては、アルミナ粉をはじめとする高熱伝導性を有する無機充填剤を添加し、二本ロール、ニーダーまたは押出し機等の加熱溶融混練機で調製する方法が用いられるが、これらの無機充填剤は、硬度が高く、一般的に破砕状の形状をしているため、混練時に混練機のロール表面やスクリュ表面が著しく摩耗し、樹脂組成物中に金属不純物が混入する問題が指摘されていた。

【0005】また一方で、パッケージが小型化になった場合、それにともない樹脂成形体の肉厚が薄くなるため、大気中の水分が樹脂成形体を通してパッケージ内部に浸入しやすくなる点も問題とされていた。

【0006】

【発明が解決しようとする課題】本発明は、前記問題点を解決するために提案されたものであって、無機充填剤を含有したエポキシ樹脂組成物について、従来のものよりも熱伝導率が高く、耐湿性に優れ、さらに樹脂組成物の調製の際、混練機のロール表面やスクリュ表面を組成物中の無機充填剤によって摩耗させることが少なく、金属不純物の発生を抑えた樹脂製中空パッケージ用に好適なエポキシ樹脂組成物を提供し、今後ますます高画素化、小型化するCCD、CMOS等の固体撮像素子を収納するための樹脂製中空パッケージを提供することにある。

【0007】

【課題を解決するための手段】本発明者らは、上記課題を解決するため、種々検討を行った結果、本願発明を完成するに至った。即ち、本発明は、

① エポキシ樹脂、硬化剤、硬化促進剤、球状アルミナ粉および低密度球状シリカ粉を含み、加えて球状溶融シリカ粉、破砕シリカ粉および窒化アルミニウム粉から選ばれる少なくとも1種を含むエポキシ樹脂組成物であって、上記球状アルミナ粉は下記（1）式で求めた球形度が0．9以上、平均粒径が0．1μm以上30μm未満、かつ組成物の全質量に対する含有量が10質量％以上80質量％以下であり（但し、球状アルミナ粉および低密度球状シリカ粉と、球状溶融シリカ粉、破砕シリカ粉、窒化アルミニウム粉から選ばれる少なくとも1種との合計の含有量は、組成物の全質量に対して95質量％

以下である。）、該組成物の硬化物の熱伝導率が１W／m・K以上であることを特徴とするエポキシ樹脂組成物＊＊を提供する。

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【０００８】❷　前記低密度球状シリカ粉が、１－ブタノールを媒体として測定した密度が２．１０g／cm³未満、吸湿率が３％以上、かつ平均粒径が０．１μm以上３μm未満であり、全組成物中に１質量％以上３０質量％以下含有されることを特徴とする前記❶に記載のエポキシ樹脂組成物は本発明の好ましい態様である。

【０００９】また本発明は、

❸　前記❶または❷に記載のエポキシ樹脂組成物からなることを特徴とする半導体素子収納中空パッケージ用エポキシ樹脂組成物を提供する。

【００１０】また本発明は、

❹　前記❶または❷に記載のエポキシ樹脂組成物から成形されたことを特徴とする半導体素子収納中空パッケージを提供する。

【００１１】

【発明の実施の形態】以下に本発明を詳細に説明する。本発明のエポキシ樹脂組成物は、エポキシ樹脂、硬化剤、硬化促進剤、球状アルミナ粉および低密度球状シリカ粉を含み、加えて球状溶融シリカ粉、破砕シリカ粉および窒化アルミニウム粉から選ばれる少なくとも１種を含み、硬化物の熱伝導率が１W／m・K以上であるエポキシ樹脂組成物である。

【００１２】＜エポキシ樹脂＞本発明のエポキシ樹脂としては、ビスフェノールA型、ビスフェノールF型、ビスフェノールAD型の各エポキシ樹脂、フェノールノボラック型エポキシ樹脂、オルソクレゾールノボラック型エポキシ樹脂、ナフタレン骨格含有エポキシ樹脂、ビフェニル骨格含有エポキシ樹脂が好適に用いられ、これらのいずれか１種類を単独で使用しても、あるいは２種類以上を適当な比率で併用してもよい。これらのエポキシ樹脂のエポキシ当量は３００（g／eq）以下が好ましく、さらには３００（g／eq）以下１００（g／eq）以上が好ましい。本発明において、エポキシ樹脂の全樹脂組成物中における配合量は、通常２質量％以上３０質量％以下であり、とりわけ３質量％以上１５質量％以下の範囲内にあるのが好ましい。

【００１３】＜硬化剤＞本発明で用いられる硬化剤としては、上記エポキシ樹脂と硬化反応するものであれば特に制限無く使用することができるが、なかでもフェノール樹脂が好ましく、具体的には、フェノールノボラック樹脂、アラルキルフェノール樹脂が挙げられる。また、ジアミノジフェニルメタン、ジアミノジフェニルスルホン、m－フェニレンジアミン等のアミン類、無水フタル酸、無水テトラヒドロフタル酸、無水ヘキサヒドロフタル酸等の酸無水物、イソフタル酸ジヒドラジド、アジピン酸ジヒドラジド等の酸ジヒドラジド、ジシアンジアミド、三フッ化ホウ素等が好適なものとして挙げられる。※

※【００１４】硬化剤の配合量は、耐湿性および機械的特性の観点から、エポキシ樹脂のエポキシ基に対する化学当量比が、０．５～１．５の範囲にあることが好ましく、さらには０．７～１．２の範囲にあることが好ましい。

【００１５】＜硬化促進剤＞本発明で用いられる硬化促進剤としては、前記エポキシ樹脂と硬化剤との架橋反応を促進するものが用いられる。その具体的な例としては、２－メチルイミダゾール、２－エチル－４－メチルイミダゾール、２－エチル－４－メチルイミダゾールアジン等のイミダゾール類；トリフェニルホスフィン、トリ（p－メチルフェニル）ホスフィン等の有機ホスフィン類；１，８－ジアザシクロ（５，４，０）ウンデセン－７（以下DBUという。）フェノール塩、フェノールノボラック塩、炭酸塩などのDBU誘導体；式Ar－NH－CO－NR_2、Ar－（NH－CO－NR_2）$_2$（Arは置換または非置換のアリール基、Rは同一または異なっていてもよい置換または非置換のアルキル基である。）で表される尿素誘導体が挙げられる。

【００１６】硬化促進剤は、エポキシ樹脂１００質量部に対して、０．１質量部以上２０質量部以下で配合されることが好ましく、さらには０．１質量部以上１０質量部以下の割合で配合されることが好ましい。

【００１７】＜無機充填剤＞本発明に用いられる無機充填剤としては、球状アルミナ粉および低密度球状シリカ粉を含み、加えて球状溶融シリカ粉、破砕シリカ粉および窒化アルミニウム粉から選ばれる少なくとも１種を含む。

【００１８】本発明で用いられる球状アルミナ粉は、下記（１）式で求めた球形度が０．９以上のものであり、平均粒径が０．１μm以上３０μm未満のものであり、好ましくは０．５μm以上３０μm未満のものである。球形度＝粒子の投影面積／粒子の投影周囲長と同じ円周を持つ真円の面積…(1)球形度を求めるには、走査型電子顕微鏡と画像解析装置を用い、電子顕微鏡で得られたSEM写真の画像解析を行って測定する。測定粒子数は１００個以上である。平均粒子径はレーザー回折式粒度分布測定機により測定した。また、球形度がこの範囲のものであれば、複数の種類のアルミナ粉を用いてもよい。この場合において、複数の種類のアルミナ粉を混合したアルミナ粉の平均粒径は上記の範囲内である。最大粒径は２００μm以下であることが好ましい。

【００１９】このような、球状アルミナ粉を用いることにより、エポキシ組成物の熱伝導率が高くなるとともに、樹脂組成物の調製の際、二本のロール、ニーダーまたは押出機等の混練機のロール表面やスクリュ表面を摩耗させることが少なく、従来使用されている破砕状アル

ミナ粉に比べて金属不純物の発生を大幅に低減することができる。本発明においては、球状アルミナ粉の組成物の全質量に対する含有量は、１０質量％以上８０質量％以下であり、好ましくは２５質量％以上８０質量％以下である。但し、球状アルミナ粉および低密度球状シリカ粉と、球状溶融シリカ粉、破砕シリカ粉、窒化アルミニウム粉から選ばれる少なくとも１種との合計の含有量は、組成物の全質量に対して９５質量％以下であり、好ましくは３０質量％以上９５質量％以下であることが好ましい。この範囲であると、エポキシ樹脂組成物の成形性に優れるとともに、機械的強度等の樹脂硬化物の特性が維持される。

【００２０】本発明で用いられる低密度球状シリカ粉は、１－ブタノールを媒体として測定した密度が２．１０ｇ／ｃｍ^{3}未満であるものが好ましく、さらには１．５５ｇ／ｃｍ^{3}以上２．０５ｇ／ｃｍ^{3}以下であるものが好ましい。吸湿率は３％以上であるものが好ましく、さらには５％以上であるものが好ましい。また、平均粒径は、０．１μｍ以上３μｍ未満であるものが好ましく、さらには０．２μｍ以上３μｍ未満のものが好ましい。

【００２１】本発明において、低密度球状シリカ粉の密度は、次の方法で測定した。ＪＩＳＲ３５０３で規定された容量５０ｍｌのワードン型比重瓶（質量m_0）に、十分に粉砕し乾燥したシリカ約５ｇを入れ精秤した。この時の比重瓶とシリカの合計質量をm_Sとした。予め脱気した１－ブタノール約１０ｍｌを加え、超音波撹拌を３０分間行った。次いで、この比重瓶を減圧デシケーターに移し、少なくとも３０ｍｍＨｇの真空度中に１５分間置き、シリカに１－ブタノールを十分浸透させた。次に１－ブタノールを比重瓶に満たし、蓋をし、２５℃の恒温相に１５分間浸漬放置させた後、質量を測定した。この時の比重瓶とシリカと１－ブタノールの合計質量をm_{S1}とした。

【００２２】また、これとは別に、比重瓶の体積を測定する目的で次の操作を行った。比重瓶に予め脱気処理した水を満たし、蓋をし、２５℃の恒温水槽に１５分間浸漬放置させた後、質量を測定した。この時の比重瓶と水の合計質量をm_1とした。そして、次の計算法により、２５℃におけるシリカの密度ρ_Sを算出した。

$\rho_S=(m_S-m_0)/\{V-(m_{S1}-m_S)/\rho_B\}$

但し$V=(m_1-m_0)/\rho_W$

ここで、

m_0：比重瓶の質量（ｇ）

m_S：比重瓶とシリカの合計質量（ｇ）

m_{S1}：比重瓶とシリカと１－ブタノールの合計質量（ｇ）

m_1：比重瓶と水の合計質量（ｇ）

ρ_S：２５℃におけるシリカの密度（ｇ／ｃｍ^3）

ρ_B：２５℃における１－ブタノールの密度（０．８０６０ｇ／ｃｍ^3）

ρ_W：２５℃における水の密度（０．９９７０４７ｇ／ｃｍ^3）

Ｖ：比重瓶の体積（ｃｍ^3）

である。なお、測定は２回繰り返し、その平均値を算出した。

【００２３】本発明において、低密度球状シリカ粉の吸湿率は、次の方法で測定した。十分に乾燥したシリカ約５ｇを容器に入れ、精秤し、この時の質量をW_0とする。次いで、この容器を６０℃、９０％ＲＨ（相対湿度）の恒温恒湿槽に入れ、２４時間放置し、この時の質量をW_1とする。このW_0、W_1から次の式で吸湿率を計算した。

吸湿率（％）＝｛（W_1-W_0）／W_0｝×１００

【００２４】本発明において、低密度球状シリカ粉の平均粒径は下記の方法によって測定した。シリカ５ないし５０ｍｇを、分散媒１０ないし２０ｍｌに超音波撹拌機を用いて分散させた。分散媒としては、粒径に応じて、水またはポリエチレングリコールを使用した。分散液をセルに移し、気泡を除いて蓋をし、遠心沈降法粒度分布測定機（堀場製作所製ＣＡＰＡ－７００型）にかけた。測定機の回転速度は、粒径に応じて５００ないし５０００ｒｐｍとした。測定機により算出されたＤ（MEDIAN）値を平均粒径とした。また、本発明の平均粒径測定においては、粒径に応じてこの他に電子顕微鏡法、レーザー回折法でも測定した。

【００２５】このような低密度球形シリカ粉を用いることにより、樹脂製中空パッケージが小型化され成形体の肉厚が薄くなっても、大気中の水分のパッケージへの進入に対して耐湿性を有する。低密度球状シリカ粉の全組成物中の含有量は、１質量％以上３０質量％以下であることが好ましく、さらには、１質量％以上２０質量％以下であることが好ましい。

【００２６】球状溶融シリカ粉は、球状の溶融シリカ粉であればその球形度は特に限定されない。平均粒径は０．１μｍ以上４０μｍ未満のものが好ましく、さらには１μｍ以上３５μｍ未満のものが好ましい。破砕シリカ粉は、溶融シリカであっても結晶シリカであってもよい。平均粒径は０．１μｍ以上３５μｍ未満のものが好ましく、さらには１μｍ以上３０μｍ未満のものが好ましい。窒化アルミニウム粉の平均粒径は、０．１μｍ以上３０μｍ未満のものが好ましく、さらには０．１μｍ以上２０μｍ未満のものが好ましく用いられる。これらの球状溶融シリカ粉、破砕シリカ粉、窒化アルミニウム粉の無機充填材は、硬化物の熱伝導率をコントロールするために選択され、配合量が調整される。

【００２７】＜その他の配合剤＞本発明においては、必要に応じ、本発明の目的を損なわない範囲で、その他の無機充填材としてフェライト粉、水酸化アルミニウム粉、炭酸カルシウム粉等を配合させることができる。また、離型剤として、モンタン酸、ステアリン酸、ベヘニ

ン酸、オレイン酸等の高級脂肪酸のエステルワックス；カルナバろう（カルナバワックス）；ベヘニン酸亜鉛、オレイン酸亜鉛、ステアリン酸マグネシウム、ステアリン酸バリウム、ステアリン酸アルミニウムなどの高級脂肪酸の金属塩；ジンクステアレート等の金属石鹸を配合させることができる。これらは単独であっても、混合して用いても差し支えない。

【００２８】また、これら以外に、本樹脂組成物に対して必要に応じて、シランカップリング剤、ブロム化エポキシ樹脂、三酸化アンチモンなどの難燃剤、カーボンブラック、フタロシアニンなどの着色剤、低応力化剤を配合しても差し支えない。本発明では、これらの全材料をヘンシェルミキサー等の通常用いられる混合機により混合した後、二本ロールやニーダー等により加熱混練し、続いて冷却、粉砕することで目的とするエポキシ樹脂組成物を得る。

【００２９】このエポキシ樹脂組成物は、ＣＣＤ、ＣＭＯＳ等の固体撮像素子を収納するための中空パッケージ用として優れた適性を示すものであるが、エポキシ樹脂組成物が一般的に使われる半導体封止や電子部品等にも使用し得ることはもちろんである。

【００３０】＜中空パッケージ＞本発明のエポキシ樹脂組成物によって成形される中空パッケージは、通常、図１に示すように、上方が開口した箱形の形状１からなり、その上面はガラスや透明なプラスチックなどの蓋材２によって、接着剤３を介して密封される。さらにパッケージ中央凹部にはアイランド４が設けられ、そこに載置された半導体素子５が、ボンディングワイヤー６を介してリードフレームと連結される。リードフレームはパッケージ成形時にインサート成形により一体成形され、外部リード７と内部リード８とがパッケージ内に封入されたリードフレームを介して連結されている。

【００３１】本発明の半導体素子収納中空パッケージは、前記のエポキシ樹脂組成物を用いて、射出成形法、トランスファー成形法などの任意の成形方法で成形されるが、トランスファー成形法が好ましく採用される。トランスファー成形方法による場合、圧力１～５０×10^6Ｐａ（１０～５００ｋｇ／ｃｍ^2）、温度１５０～２００℃、時間１～５分間の成形条件によって成形することができる。

【００３２】

【実施例】以下、本発明の優れた効果を実施例により説明するが、本発明は実施例に限定されるものではない。

【００３３】（実施例１～５、比較例１～４）

表１に示す全原料

オルソクレゾールノボラックエポキシ樹脂＜エポキシ樹脂＞：日本化薬(株)製、ＥＯＣＮ－１０２０－７０、エポキシ当量＝２０５ｇ／ｅｑ、

アラルキルフェノール樹脂＜硬化剤＞：三井化学(株)製、ミレックスＸＬＣ－３Ｌ、

イミダゾール＜硬化促進剤＞：四国化成(株)製、２Ｅ４ＭＺ－ＡＺＩＮＥ、

球状アルミナ粉(1)＜無機充填材＞：平均粒径９．０μｍ、密度３．５７ｇ／ｃｍ^3、球形度０．９２、

球状アルミナ粉(2)＜無機充填剤＞：(a)平均粒径４５μｍ、密度３．９８ｇ／ｃｍ^3、球形度０．９２のものと(b)平均粒径４μｍ、密度３．９８ｇ／ｃｍ^{3}のものと(c)平均粒径０．７μｍ、密度３．９８ｇ／ｃｍ^{3}のものとの３種類を(a)／(b)／(c)＝５／３／２の割合（質量比）で混合した、平均粒径１４μｍ、密度３．９８ｇ／ｃｍ^{3}の球状アルミナ粉、

破砕状アルミナ粉＜無機充填材＞：平均粒径１２．０μｍ、密度３．９８ｇ／ｃｍ^3、

低密度球状シリカ粉＜無機充填材＞：平均粒径（遠心沈降法粒度分布測定機）１．０μｍ、密度（媒体１－ブタノール）１．７８ｇ／ｃｍ^3、吸湿率１１．８％、

球状溶融シリカ粉＜無機充填材＞：平均粒径２６．０μｍ、密度２．２１ｇ／ｃｍ^3、

破砕シリカ粉＜無機充填材＞：平均粒径１４．５μｍ、密度２．６５ｇ／ｃｍ^3、

窒化アルミニウム粉＜無機充填材＞：平均粒径０．５μｍ、密度３．２６ｇ／ｃｍ^3、（低密度球状シリカ粉以外の無機充填材の平均粒径は、ＣＩＬＡＳ社製レーザー回折式粒度分布測定装置Ｇｒａｎｕｌｏｍｅｔｅｒ ＭＯＤＥＬ９２０により測定し、密度には、ＪＩＳで定められた方法に従って、ピクノメーターで測定した比重の値を示した。）

モンタン酸ワックス＜離型剤＞：クラリアントジャパン(株)製、リコワックスＯＰ、

シランカップリング剤＜難燃剤＞：信越化学工業(株)製、ＫＢＭ－４０３、

ブロム化エポキシ樹脂＜難燃剤＞：日本化薬(株)製、ＢＲＥＮ－Ｓ、エポキシ当量＝２８５ｇ／ｅｑ、

三酸化アンチモン＜難燃剤＞：日本精鉱(株)製、ＰＡＴＯＸ－Ｍ、

カーボンブラック＜着色剤＞：三菱化学(株)製、＃４５、

を、表中に記載の重量部の割合でヘンシェルミキサーにより混合した後、温度９０～１１０℃の二本ロールで加熱混練し、次いで冷却粉砕してエポキシ樹脂組成物を得た。この組成物を用いて、以下の評価方法により物性を測定した。結果を表１に併せて示した。

【００３４】＜評価方法＞

（１）スパイラルフロー

ＥＭＭＩ１－６６規格に準じた内部がスパイラル状になった金型を用い、トランスファー成形にて、金型温度１５０℃、実効圧力６．９×10^6Ｐａ（７０ｋｇｆ／ｃｍ^2）で成形し、１８０秒間硬化した時の金型内での流動した長さを測定した。

【００３５】（２）熱伝導率

京都電子工業(株)製の迅速熱伝導率計を用いて測定した。まず、前記のようにして調製したエポキシ樹脂組成物を１０５mm(L)×５５mm(W)×１５mm(H)のサイズに成形し、この成形体を２３℃の雰囲気中に１２時間以上放置した。次に、迅速熱伝導率計のプローブを成形体に乗せ、１分後の値を読み取り熱伝導率とした。

【００３６】（３）金属不純物濃度

前記のように調製したエポキシ樹脂組成物を、Ｌｅｅｍａｎ Ｌａｂｓ社製誘導結合プラズマ発光分光分析装置を用いて、不純物として組成物中に含まれるＦｅ濃度を測定した。このＦｅ濃度を、混練時の混練機表面の摩耗度合の目安とした。

【００３７】（４）金型摩耗性

金型摩耗性の評価方法は、各社から提案されているが、測定に長時間要するものが多いため、促進法として、アルミニウム製金型に対する摩耗試験を行った。具体的には、図2に示す金型を用い、前記のように調製したエポキシ樹脂組成物を９０℃に加熱した金型に投入後、7.8×10^6Ｐａ（８０ｋｇｆ／ｃｍ^2）の圧力で加圧し、アルミニウム製ノズルの直径２mmの先端孔から１９ｃｃ吐出させた。その後、ノズル先端孔の内径を三次元座標測定機で測定し、組成物を吐出させたことにより生じた先端孔の内側の摩耗量（体積）を算出した。この値も上記（３）金属不純物濃度と同様、混練機表面の摩耗度合の判定基準とした。

【００３８】（５）比熱

中空パッケージの状態では、プローブ法による熱伝導の測定が不可能であるため、成形品の比熱でパッケージとしての熱伝導性の目安とした。前記段落番号［００３１］の中空パッケージ成形条件によって成形した成形品から、寸法が約３mm×３mmの大きさで、重量が約５ｍｇの試験片を切り出し、パーキンエルマー社製ＤＳＣ－７を用いて測定した。比熱は、常温から１０℃／分の速度で昇温させ、４０℃の時の値を示した。

【００３９】（６）耐湿性

前記のように調製したエポキシ樹脂組成物を、トランスファー成形によって、圧力7×10^6Ｐａ（７０ｋｇ／ｃｍ^2）、温度１８０℃、時間２分間の成形条件によって中空パッケージ「A」を成形する。次に中空部を気密シールするためにＵＶ硬化接着剤をガラス板に塗布した蓋材「a」を用意し、「A」に接着剤塗布側を下にした「a」を乗せ、ＵＶ硬化する。こうして、気密シールした中空の試験体を得、中空部に浸入する水分量を測定することによって耐湿性を評価した。測定は、テレビジョン学会誌（４２（９），９５９（１９８８））に記載された方法を参考にした。すなわち、試験体をプレッシャークッカー試験機に入れ、温度１２１℃、湿度１００％ＲＨの湿熱環境で１０時間暴露した。次いでガラス面を強制冷却し、中空部内の水分が結露するかどうかを調べた。プレッシャークッカーで結露が認められなかったものを○と判定した。

【００４０】

【表１】

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原料（重量部）		実施例1	実施例2	実施例3	実施例4	実施例5	比較例1	比較例2	比較例3	比較例4
オルソクレゾールノボラックエポキシ樹脂		100	100	100	100	100	100	100	100	100
アラルキルフェノール樹脂		93	93	93	93	93	93	93	93	93
ブロム化エポキシ樹脂		27	27	27	27	27	27	27	27	27
無機充填剤	球状アルミナ粉(1)	1037	518	1037	1037					
	球状アルミナ粉(2)					724				
	破砕状アルミナ粉						1037		518	
	低密度球状シリカ粉	126	126	126	126	137	126	126	126	126
	球状溶融シリカ粉	302	593				302		593	1339
	破砕シリカ粉			302		724		1339		
	窒化アルミニウム粉				302					
三酸化アンチモン		5	5	5	5	5	5	5	5	5
カーボンブラック		2	2	2	2	3	2	2	2	2
シランカップリング剤		7	7	7	7	3	7	7	7	7
イミダゾール		7	7	7	7	7	7	7	7	7
モンタン酸ワックス		3	3	3	3	3	3	3	3	3
スパイラルフロー　(cm)		72	60	48	30	23	34	29	39	77
熱伝導率 (W/m·K)		1.6	1.1	2.0	2.5	2.4	2.2	1.8	1.2	0.8
金属不純物濃度 (Fe)　(ppm)		240	180	350	380	470	1750	1130	860	200
金型摩耗量 ($\times 10^{-6}$cc)		0.44	0.39	0.58	0.65	1.04	3.50	2.70	2.10	0.40
耐湿性		○	○	○	○	○	○	○	○	○
パッケージ成形品の比熱 ($\times 10^{-1}$J/g℃)		9.28	未測定	未測定	未測定	未測定	未測定	未測定	未測定	9.95

【００４１】表１の結果より、球状アルミナ粉を配合したエポキシ樹脂組成物（実施例１～４）は、１W／m・K以上の熱伝導率を示し、パッケージ成形品の比熱も小さいことから、熱伝導性が優れている。また金属不純物の濃度も低い値を示し、金型摩耗量も、破砕アルミナ粉や破砕シリカ粉を主体とした組成物（比較例１～３）に比べ少ないことから、混練機表面のダメージが少ないことが分かった。さらに耐湿性も良好な結果を示した。比較例４は、球状シリカ粉のみの組成物であり、金属不純物濃度と金型摩耗量は少ないものの、熱伝導率が１W／m・Kを下まわった。

【００４２】

【発明の効果】本発明のエポキシ樹脂組成物は、耐湿性に優れ、熱伝導率が高く、ＣＣＤやＣＭＯＳ等の固体撮像素子を収納するための樹脂製中空パッケージに適している。さらに、破砕状のアルミナをはじめとする高熱伝導性を与える無機充填剤の問題点とされていた、組成物を調製する際の混練機ロール表面やスクリュ表面の摩耗と、金属不純物の混入の点を著しく改善することができる。

＊【図面の簡単な説明】

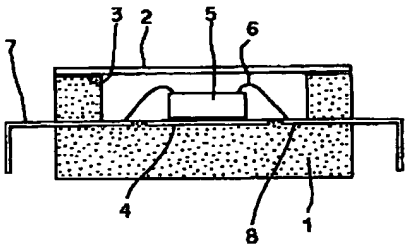
【図１】本発明のエポキシ樹脂組成物によって成形された中空パッケージの一例を示す断面図である。

【図２】本発明の実施例で用いた金型摩耗性の測定方法を説明するための概略図である。

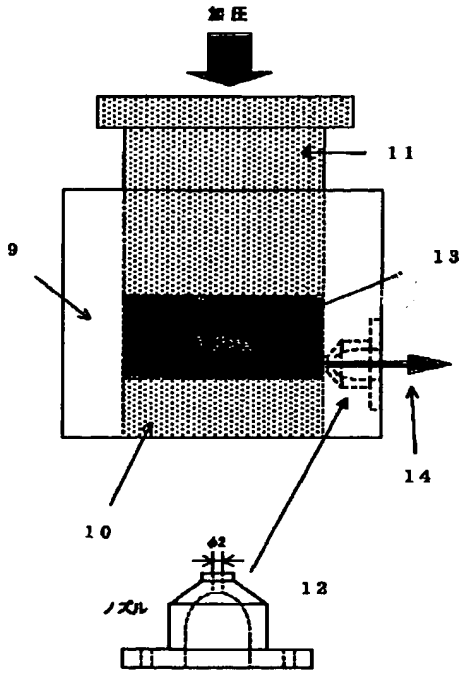
【符号の説明】

１　中空パッケージ
２　蓋材
３　接着剤
４　アイランド
５　半導体素子
６　ボンディングワイヤー
７　外部リード部
８　内部リード部
９　円筒金型
１０　中子（固定型）
１１　中子（可動型）
１２　アルミニウム製ノズル
１３　エポキシ樹脂組成物
１４　押し出されるエポキシ樹脂組成物

【図1】



【図2】



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